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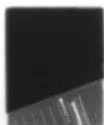
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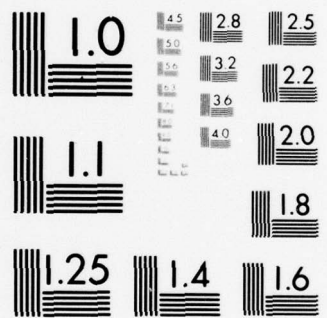
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TECHNICAL REPORT 7902

FIXATION OF TOBYHANNA ARMY DEPOT ELECTROPLATING WASTE SAMPLES  
BY ASPHALT ENCAPSULATION PROCESS

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JANUARY 1979

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Electroplating waste samples from Tobyhanna Army Depot, PA, and other synthetically prepared samples of hazardous waste were fixed by the WPC-VRS process of Werner & Pfleiderer Corp. (asphalt micro-encapsulation) and evalu- ated by using the modified Wisconsin leaching test. It was found that the process provides satisfactory attenuation to leaching of heavy metal ions, hexavalent chromium, and cyanide. The presence of complexing ions like cyanide, ammonia, and high pH, however, seems to adversely affect the performance of the		

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CONT

20. Abstract (Cont'd)

process, slightly increasing the leaching of zinc, copper and cadmium. Excepting these metals, the concentrations of other metals in the leachates generated are within the limits set by the proposed Pennsylvania State Regulations and/or USEPA Standards.

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## INTRODUCTION

### Hazardous Wastes: Definition and Occurrence

The waste materials generated by various industrial processes and operations can be phenomenologically classified as "Hazardous Wastes" when they pose an immediate or potential risk to the health and well-being of plant, animal and human life by virtue of certain of their properties, which include flammability, chemical and physical reactions, infectiousness, radioactivity and toxicity. The survey conducted by the United States Environmental Protection Agency (USEPA),<sup>1</sup> under the provisions of the Resources Conservation and Recovery Act (RCRA) 1970, Section 212, among 14 nationwide industrial categories excepting radioactive waste, reveals that 29 million tons of a total of 200 million tons of waste can be categorized as hazardous, and that hazardous waste will be generated to the extent of 38 million tons by the year 1983. Of this, about 5 million tons are produced by the electroplating industry alone.

The disposal methods employed for these wastes can be (1) ocean dumping, (2) river and stream dumping, (3) deep well or mine burial, (4) temporary storage or lagooning, (5) use of landfills and (6) incineration followed by use of landfills. Due to the Marine Protection Research and Sanctuaries Act of 1972 as amended (PL-93-254, 1974), ocean and river dumping has been almost eliminated, and of the total 29 million tons of hazardous waste, more than 83% is disposed of in landfill sites and only 17% of it is subject to pretreatment and recovery. According to the Federal Water Pollution Control Act (Clean Water Act) as amended (1977),<sup>2</sup> most of these hazardous wastes may require recovery or pretreatment and filtration of aqueous wastes before disposal.<sup>3</sup> This is because of the intrinsic difficulty involved in the hydrogeologic isolation of landfills, which is needed to prevent aquifer degradation. Figures on the total hazardous waste generated in Army Depots and installations were not available at the time of this report. However, it could be estimated that this amounts to only a small fraction of the total for the nation. The present investigation, moreover, is concerned only with the electroplating and paint-removal waste from Tobyhanna Army Depot (TOAD), which produces about 30,000 gallons per year of hazardous waste with a solids content of 5-20%. The heavy metals and cyanide contained in these wastes are hazardous and must be effectively removed from effluent water and fixed before disposal. Large-scale industries have separate unitary installations to achieve this, using existing technology. However, for the small scale of TOAD's operations, such installations would be prohibitively expensive; therefore, research was necessary to discover less expensive and possibly more effective methods of fixing and disposing of these wastes.

### Electroplating Wastes

In the pretreatment of electroplating wastes, the batches containing hexavalent chromium and those containing cyanide are segregated and separately treated to reduce hexavalent chromium to the trivalent state and totally destroy cyanide in two stages by alkaline chlorination. Then the total waste is limed to precipitate the heavy metals. The processes are fully described by Curry,<sup>4</sup> Lavin and Lavin,<sup>5</sup> and Werner.<sup>6</sup> The methodology for fixing the liquid waste or separated and filtered solid waste consists of production of a solid inert matrix in which pollutant components remain embedded and are attenuated in the leaching process.<sup>7</sup> Many types of materials, including fly ash,<sup>7</sup> portland cement,<sup>7</sup> sodium silicate,<sup>8</sup> polyethylene,<sup>9</sup> nylon,<sup>9</sup> polybutadiene,<sup>9</sup> and asphalt,<sup>10-12</sup> have been used for solidification purposes, all with claims of good results. The integrity and stability of the solidified material are important in these processes, in addition to the leaching behavior, which is a deciding factor.

### Leachate Generation and Analysis<sup>13,14</sup>

For the evaluation of the different fixation processes, a logical, efficient and quick method of testing the behavior of fixed waste at the disposal sites is necessary. Examination of the various leaching methods summarized on behalf of the EPA indicates that any method devised for evaluating a fixing process by leaching tests should simulate the natural leachate production circumstances actually occurring at the landfill sites.<sup>13</sup> To conform to this criterion, variables such as pH, redox potential, ionic strength, buffer capacity, particle size of sample, method of agitation, and duration of test, must be properly addressed. The naturally occurring leaching medium is an aqueous solution of humic and other organic acids and carbon dioxide partially neutralized by basic materials in the soil. This makes the leachant medium acidic with high ionic and buffer strengths. The presence of reducing and oxidizing substances and of biological materials further complicates the situation. Even if these complicating factors are neglected, the leaching medium must at least be acidic at high ionic and buffer strengths. Distilled or deionized water may be used for obtaining data, but such leachants are useful only to compare different fixation processes, not for the evaluation of the absolute performance of an individual fixation process. The modified Wisconsin Test,<sup>13</sup> in which the most pertinent of the above factors were considered, was used in the present investigation, and is discussed in detail in the experimental section of this report.

The hazardous wastes at Tobyhanna Army Depot were examined by the Army Corps of Engineers through the contractors, A.E. Peters Associates.<sup>8</sup> They made an extensive investigation and recommended their "Chem-Fix Process" for fixation of the waste, to be followed by disposal in 55-gallon drums in approved sites. The "Chem-Fix Process" consists of solidification of the waste slurry, after liming, with portland cement

and sodium silicate. Samples containing hexavalent chromium and cyanide have to be treated separately for elimination of these components, the leachability of which cannot be attenuated by the process. Special leaching column test methods were devised for testing the "Chem-Fix Process," with deionized water as an eluent (i.e., leachant). The test results showed uniformly less than 0.1 ppm of each heavy metal leached by the eluent in all cases. The percentage leaching and cumulative percentage leaching of all metals was not evaluated in that work.

Further, USAEHA workers<sup>15</sup> modified the "Chem-Fix Process," by increasing the solids content, using calcium sulfite to reduce  $\text{Cr}^{+6}$  to  $\text{Cr}^{+3}$  and limiting the sodium content of the total mixture in order to ensure solidification of the final product. As above, the final solid material was subjected to leaching tests with distilled water of unspecified pH as a leachant at a sample-to-leachant ratio of 1:4, with use of a reciprocating shaker, for 48 hours. The amounts of metals leached ranged from 0.2% to 0.8% of the total, and the concentration of the metals (Cr, Cu, Cd, Pb, and Sn) in the leachate averaged from 5.27 to 8.69 mg/l. The poor solubilizing power of unbuffered distilled water used as a leachant is reflected in the extremely low levels of metals leached in this test. The implications of these results are questionable, since hydroxides of the heavy metals are not irreversibly bound in the matrix of cement concrete, and are therefore liable to dissolve in the low-pH leachants of landfills.

#### Asphalt Fixation

Asphalt fixation of waste salts, especially radioactive wastes, is one of the cheapest, most efficient methods of fixation.<sup>10,11</sup> The radioactive salts, which are generally soluble and inorganic, are micro-encapsulated with molten asphalt after evaporation of water and micronization of the residue. Even emulsified asphalt can be used for the purpose. The WPC-VRS process<sup>12</sup> of Werner & Pfleiderer Corp. is a special asphalt-fixing process, and has been used for the disposal of radwastes in Europe for the last decade. The standard leaching test results from all these fixation processes show that extremely small quantities of heavy metals are leached from the samples. Therefore, heavy metal and cyanide wastes from the electroplating industry are relevant and logical subjects for application of the asphalt fixation process. The performance of the WPC-VRS asphalt-fixing process was therefore investigated by application to actual electroplating waste samples from Tobyhanna Army Depot and to synthetically prepared samples simulating the wastes generated at various Army Depots. The results of the investigation are presented in this report.



## OBJECTIVE

This experimental study was undertaken at the request of USAEHA<sup>16</sup> to evaluate the methods of fixation of industrial hazardous wastes containing toxic heavy metals. An investigation had already been carried out by A.E. Peters Associates,<sup>8</sup> in order to solve the problem of disposing of electroplating wastes at Tobyhanna Army Depot in order to conform to the requirements of the state government, and a report had been published in 1977.<sup>8</sup> A USAEHA team of workers continued to investigate the cementation and solidification process of A.E. Peters Associates, and made their final recommendations in 1978. In view of these studies, the present work was confined to fixation of Tobyhanna electroplating waste by the asphalt micro-encapsulation process, and its evaluation for comparison with other "Chem-Fix Processes" investigated by the Army Corps of Engineers and by the USAEHA.

## EXPERIMENTAL

### Procurement and Conditioning of Waste Sludge Samples

Tobyhanna Army Depot electroplating waste water had previously been limed to precipitate heavy metals without segregating chrome- and cyanide-containing wastes and without reduction of hexavalent chromium or destruction of cyanide. Two samples, 1 gallon each, were collected at two different points in the form of thick sludge with about 37% to 50% solids content. (Both samples contained large amounts of hexavalent chromium and cyanide, as evidenced later.) Two more samples were synthetically prepared in the laboratory to simulate pollutant compositions similar to those that would most probably be encountered in various Army Depots. The compositions of these samples are given in Tables 1 and 2. All four samples were made into slurries with the consistency most convenient for asphalt-fixing operations to be conducted at Werner and Pfleiderer Corp.'s Industrial Laboratory (Waldwick, NJ).

### Asphalt Fixation of Waste Samples

Asphalt fixation was carried out at the Werner and Pfleiderer Corp. facility in Waldwick, NJ by their WPC-VRS process. The process machinery consisted of a motor-driven twin-screw co-rotating extruder with incorporated pulverizing, mixing and kneading attachments, and a hopper to feed the waste and molten asphalt. A separate unit for melting and pumping asphalt to the hopper and a unit for evaporating off water and volatiles from the extruder and condensing them separately were provided. The wastes, introduced in a thin stream, were conveyed along with asphalt by the twin screws, pulverized to 20-micron size, coated, mixed with asphalt, and agitated to assist passage of water vapor to the condenser. The fixed sample was then delivered into sample containers at the final outlet. The dry waste and asphalt were in a weight ratio of 1:1 in the fixate, which was sticky and semisolid to touch.

TABLE 1. SYNTHETIC SAMPLE NO. 1<sup>a</sup>

	mg/kg	Metal
Cadmium iodide	300	Cd <sup>+2</sup>
Chromium chloride	800	Cr <sup>+3</sup>
Chromium trioxide	1000	Cr <sup>+6</sup>
Ferric nitrate	1400	Fe <sup>+3</sup>
Lead acetate	6	Pb <sup>+2</sup>
Nickel acetate	8	Ni <sup>+2</sup>
Sodium cyanide	500	CN <sup>-1</sup>
Zinc oxide	850	Zn <sup>+2</sup>

a. The sample was made to 1 kg by the addition of CaSO<sub>4</sub> (anhydrous).

#### Analysis of the Raw and Fixed Wastes<sup>12</sup>

A sample of hazardous waste (2.5 g) was accurately weighed and digested on low heat with 25 ml of concentrated nitric acid in a 600-ml beaker for 30-45 min. The mixture was then cooled and mixed with 10 ml of 72% perchloric acid and gently boiled until colorless, and diluted to volume in a 100-ml or a 250-ml volumetric flask. In the case of asphalt-fixed samples, the sample-nitric acid-perchloric acid mixtures were each digested for several hours with an additional 10 ml of perchloric acid until colorless and then diluted to final volume. The solutions were preserved in glass containers protected from light by aluminum foil in a refrigerator at 4°C until they were analyzed for their metal contents.

Analyses were carried out for iron, zinc, copper, cadmium, lead chromium (total), silver, arsenic and mercury with the aid of a Perkin-Elmer Model 403 Atomic Absorption Spectrophotometer equipped with a Deuterium Background Corrector, a Perkin-Elmer HGA-2000 Graphite Furnace, accessories for the air-acetylene flame, and a model 056 recorder.<sup>17</sup> The air-acetylene flame was employed for samples of high metal concentrations and the graphite furnace for metal concentration below the sensitivity attainable with an air-acetylene flame.

TABLE 2. SYNTHETIC SAMPLE NO. 2<sup>a</sup>

Chemical Compound	mg/kg of Metal	
Aluminum ammonium sulfate	1000	Al <sup>+3</sup>
Barium chloride	1000	Ba <sup>+2</sup>
Cadmium iodide	1000	Cd <sup>+2</sup>
Chromium chloride	1000	Cr <sup>+3</sup>
Chromium trioxide	1000	Cr <sup>+6</sup>
Curic chloride	1000	Ca <sup>+2</sup>
Ferric nitrate	1000	Fe <sup>+3</sup>
Lead acetate	1000	Pb <sup>+2</sup>
Magnesium sulfate	1000	Mg <sup>+2</sup>
Manganese chloride	1000	Mn <sup>+2</sup>
Mercury chloride	1000	Hg <sup>+2</sup>
Nickel acetate	1000	Ni <sup>+2</sup>
Selenium (powder)	1000	Se
Silver sulfate	1000	Ag <sup>+1</sup>
Sodium arsenate	1000	As <sup>+5</sup>
Sodium cyanide	1000	CN <sup>-1</sup>
Tin (powder)	1000	Sn
Zinc oxide	1000	Zn <sup>+2</sup>

a. The sample was made to 1 kg by the addition of calcium sulfate (anhydrous).

Electrodeless discharge lamps (EDL) were used when available, otherwise Perkin-Elmer Intensitron<sup>®</sup> hollow cathode lamps were used. All mercury analyses were carried out with the Perkin-Elmer Mercury Analysis System (cold vapor trap). Hexavalent chromium was determined by use of a Technicon AutoAnalyzer,<sup>18</sup> with s-diphenyl carbazide as a color-forming agent, at 550 nm. The soluble cyanide contents<sup>19,20</sup> were also determined by use of an AutoAnalyzer with chloramine T-barbituric acid-pyridine reagents after a digestion/distillation stage had isolated cyanide from its metallic complexes.



### Leachate Generation<sup>9,20</sup>

The modified Wisconsin procedure,<sup>13</sup> with a leachant consisting of 49.21 g/l acetic acid and 39.21 g/l sodium acetate at pH = 4.5, was adopted for this study. Raw or fixed sample (28.6 g) was ground to size (9.5 mm diameter particles), placed in a closed glass container with 200 ml eluent, and agitated with a wrist-action shaker for 24 hours. The mixture was then filtered through a 0.45 micron filter. Two hundred ml of fresh leachant was added to the residue and the process was repeated for an additional 24 hours. The leachant filtrates (leachates) were combined, for a total of 400 ml, for the metal and cyanide analyses. The ionic strength and buffer capacity of the original Wisconsin leachant<sup>21</sup> were increased according to the Minnesota procedure<sup>13</sup> and two of the components, ferrous sulfate and pyrogallol, which contribute to the redox potential and complexing capacity, were omitted to simulate natural landfill leachates more closely. The further exhaustive extractions by leachant portions recommended by Wisconsin procedure were omitted after the second extraction. The modified Wisconsin test used in this investigation has been claimed<sup>13</sup> to conform more closely to natural landfill leachants than any of the tests so far investigated. The percentage metallic contents leached by the test procedure from the sample was calculated by use of the following formula.

$$\begin{aligned}\% \text{ metal leached} &= \frac{\text{mg/l of metal in leachate}}{\text{mg/kg of metal in sample}} \times \frac{400}{28.6} \times 100 \\ &= \frac{\text{mg/l leachate}}{\text{mg/kg sample}} \times 1400\end{aligned}$$

The cumulative metal contents leached by the process was evaluated with the following formula:

$$\begin{aligned}\% \text{ of metals leached} &= \frac{\sum \text{mg/l of metal in leachate}}{\sum \text{mg/kg of metal in sample}} \times \frac{400}{28.6} \times \frac{100}{1} \\ &= \frac{\sum \text{mg/l leachate}}{\sum \text{mg/kg sample}} \times 1400\end{aligned}$$

The evaluation of total cyanide in the raw or fixed samples could not be made, owing to the evolution and escape of cyanide in the strong acid digestion method used. However, evaluation of the soluble cyanide in the leaching test was made by the standard AutoAnalyzer procedure. Calculation of the percentage of cyanide leached was not possible because of the probable presence of adsorbed and insoluble cyanide in the samples that could not be measured by the procedures used in this investigation. However, adsorbed and insolubilized cyanide can be generally taken as "chemically fixed" in the sample.

The original asphalt properties and analysis are reported in Table 3. The levels of analytical accuracies of procedures used in the metal analysis are given in Table 4. The original metal and cyanide contents of the raw samples are in Table 5 and the percentages of metals leached from four raw and fixed samples, Tobyhanna Sample Nos. 1 and 2 and synthetic sample Nos. 1 and 2, are reported in Tables 6 through 9.

TABLE 3. THE PHYSICAL AND CHEMICAL PROPERTIES  
OF ASPHALT USED FOR FIXING HAZARDOUS  
ELECTROPLATING WASTE

Softening range	190-200°F
Solubility in $\text{CCl}_4$	99.0%
Flash point	550°F
Weight per gallon	8.3 lbs
Use Temperature	400°F $\pm$ 25°
Zn (total)	3.178 mg/kg
CN (total)	BDL mg/kg
Cd (total)	0.576 mg/kg
Pb (total)	1.556 mg/kg
Fe (total)	63.677 mg/kg
Ag (total)	0.248 mg/kg
Cr (total)	BDL mg/kg
Hg (total)	BDL mg/kg
As (total)	3.667 mg/kg
CN (soluble)	BDL mg/kg

TABLE 4. METHOD OF ANALYSIS AND DETECTION LIMITS

Element or Cyanide	Method of Analysis <sup>16-18</sup>	Detection Limit
Iron	Atomic absorption	30 µg/l
Zinc	Atomic absorption	1 µg/l
Copper	Atomic absorption	50 µg/l
Cadmium	Atomic absorption	1 µg/l
Lead	Atomic absorption	10 µg/l
Chromium (total)	Atomic absorption	25 µg/l
Chromium (hexavalent)	AutoAnalyzer	4 µg/l
Silver	Atomic absorption	6 µg/l
Mercury	Atomic absorption (cold vapor trap)	0.4 µg/l
Arsenic	Atomic absorption	20 µg/l
Cyanide	AutoAnalyzer	5 µg/l

TABLE 5. HEAVY METAL CONTENTS OF EXPERIMENTAL SAMPLES

Metals or Cyanide	TOAD No. 1 <sup>a</sup>	TOAD No. 2 <sup>a</sup>	Synthetic No. 1 <sup>a</sup>	Synthetic No. 2 <sup>a</sup>
Fe (total)	6433.049	23048.334	1127.713	1235.830
Zn (total)	1343.695	567.285	--	995.635
Cu (total)	1264.969	67.804	BDL	900.170
Cd (total)	5304.121	1246.814	281.654	1030.194
Pb (total)	3466.990	445.068	7.330	516.891
Cr (total)	101.320	78.402	1714.651	1540.464
Cr <sup>+6</sup>	24.253	102.292 <sup>b</sup>	65.464	1804.380
Ag (total)	19.824	1.995	0.049	1930.356
Hg (total)	0.323	0.247	0.947	999.327
As (total)	4.705	8.459	--	1142.767
CN <sup>-</sup> (soluble)	359.180	808.330	100.330	26.280

a. The metallic and cyanide contents are given in mg/kg in all cases.

b. The values of hexavalent chromium are higher than the total chromium because of the interference of high iron and mercury contents in the AutoAnalyzer procedures used.<sup>17</sup>

TABLE 6. LEACHING ANALYSIS OF TOBYHANNA SAMPLE NO. 1

Metal	Raw Sample Sludge Metal Content mg/kg	% Metal		Asphalt Fixed Sample Metal Content mg/kg	Leachate from a Fixed Sample Metal Content mg/l	% Metal Leached from a Fixed Sample
		Leachate from Raw Sample Metal Content mg/l	Leached from Raw Sample			
Zn (total)	1343.695	49.463	52.04	295.440	4.268	20.20
Cu (total)	1264.969	41.930	47.40	273.120	2.089	10.69
Cd (total)	5304.121	298.958	80.59	1165.700	19.792	23.74
Pb (total)	3466.990	135.816	56.02	559.120	12.766	31.93
Fe (total)	6433.049	189.658	42.16	1735.550	19.326	15.60
Ag <sup>+1</sup>	19.824	1.003	72.36	5.008	BDL	0.00
Cr (total)	101.320	4.203	58.08	1.827	0.036	27.45
Cr <sup>+6</sup>	24.253	0.926	53.453	8.802 <sup>b</sup>	0.082 <sup>b</sup>	13.04
Hg (total)	0.323	0.002	48.85	BDL	BDL	--
As (total)	4.705	0.114	34.64	7.703	0.076	13.81
CN <sup>-</sup> (soluble)	--	292.117	--	--	0.076	--
Total <sup>a</sup>	17963.249	722.073	56.276	4052.27	58.435	20.188

a. The total figures include only the metal ions (cyanide values are not included).

b. The hexavalent chromium values are higher than total chromium because of the interference of high iron content in the AutoAnalyzer procedures used.<sup>17</sup>



TABLE 7. LEACHING ANALYSIS OF TOBYHANNA SAMPLE NO. 2

Metal	Raw Sample Sludge Metal Content mg/kg	Leachate from Raw Sample Metal Content mg/l	% Metal Leached from Raw Sample	Asphalt Fixed Sample Metal Content mg/kg	Leachate from a Fixed Sample Metal Content mg/l	% Metal Leached from a Fixed Sample
Zn (total)	567.285	54.957	135.628	73.766	1.012	19.206
Cu (total)	67.804	4.438	91.634	8.872	0.589	92.944
Cd (total)	1246.810	36.710	41.220	143.014	2.048	20.048
Pb (total)	445.070	25.705	80.856	53.575	0.722	18.867
Fe (total)	23048.330	173.189	10.519	2095.120	5.456	3.646
Ag <sup>+1</sup>	1.995	0.106	74.385	1.480	BDL	0.000
Cr (total)	78.402	2.431	43.409	1.482	0.226	213.49
Cr <sup>+6</sup>	102.292 <sup>b</sup>	0.497	6.800	9.188 <sup>b</sup>	0.023	3.505
Hg (total)	0.247	BDL	0.000	0.731	0.731	--
As (total)	8.459	0.225	37.238	16.894	0.076	6.298
CN <sup>-</sup> (soluble)	--	808.330	--	BDL	BDL	--
Totals <sup>a</sup>	25566.694	298.258	16.332%	2404.122	10.883	6.337%

a. The total figures include only metal ions (cyanide values are not included).

b. The hexavalent chromium values are higher than the total chromium because of the interference of high iron content in the AutoAnalyzer procedure used.<sup>17</sup>

TABLE 8. LEACHING ANALYSIS OF SYNTHETIC SAMPLE NO. 1

Metal	Raw Sample Sludge Metal Content mg/kg	Leachate from Raw Sample Metal Content mg/l	% Metal Leached from Raw Sample	Asphalt Fixed Sample Metal Content mg/kg	Leachate from a Fixed Sample Metal Content mg/l	% Metal Leached from a Fixed Sample
Zn (total)	--	42.197	--	135.798	0.481	4.959
Cu (total)	BDL	0.378	--	BDL	0.336	--
Cd (total)	281.654	16.900	85.80	49.490	0.147	4.158
Pb (total)	7.330	0.454	88.57	4.168	0.181	60.790
Fe (total)	1127.713	23.484	29.78	1135.130	0.286	0.353
Ag <sup>+1</sup>	0.049	BDL	00.00	0.137	BDL	0.000
Cr (total)	1714.651	58.025	47.37	292.888	0.050	0.239
Cr <sup>+6</sup>	654.64	27.467	58.74	12.303	0.007	0.707
Hg (total)	0.947	0.008	11.82	0.854	0.030	49.180
As (total)	--	0.013	--	6.717	BDL	0.000
CN <sup>-</sup> (soluble)	--	100.33	--	--	BDL	--
Totals <sup>a</sup>	3786.984	125.729	46.85%	1637.485	1.518	1.298%

a. The total figures include only metal ions (cyanide values are not included).

TABLE 9. LEACHING ANALYSIS OF SYNTHETIC SAMPLE NO. 2

Metal	Raw Sample Sludge Metal Content mg/kg	Leachate from Raw Sample Metal Content mg/l	% Metal Leached from Raw Sample	Asphalt Fixed Sample Metal Content mg/kg	Leachate from a Fixed Sample Metal Content mg/l	% Metal Leached from a Fixed Sample
Zn (total)	995.635	67.370	94.730	287.400	1.012	4.930
Cu (total)	900.170	63.940	99.443	604.340	0.756	1.751
Cd (total)	1030.194	69.830	94.896	583.070	1.596	3.832
Pb (total)	516.891	14.900	40.356	343.290	0.608	2.480
Fe (total)	1235.830	57.426	65.055	1059.550	0.500	0.661
Ag <sup>+1</sup>	1930.356	0.050	0.036	1592.920	BDL	0.000
Cr (total)	1540.460	96.520	87.719	1293.100	0.364	0.394
Cr <sup>+6</sup>	1804.280 <sup>b</sup>	0.352	0.273	12.303	0.007	0.797
Hg (total)	999.330	64.312	90.097	1000.200	0.278	0.389
As (total)	1142.760	38.405	47.050	3.667	0.075	28.633
CN <sup>-</sup> (soluble)	--	26.795	--	--	0.023	--
Totals <sup>a</sup>	12122.185	473.105	54.639%	6805.92	5.224	1.075%

a. The total figures include only metal ions (cyanide values are not included).

b. The hexavalent chromium values are higher than total chromium because of the interference of high mercury contents in the AutoAnalyzer procedures used.<sup>17</sup>



## RESULTS AND DISCUSSION

The leaching test leachant used in the present work is a highly efficient solubilizing medium simulating naturally occurring leachants at landfill sites of low pH (4.5), high ionic strength and high buffer capacity.<sup>13,21</sup> The grinding of samples to 9.5 mm diameter particles and the vigorous wrist-action shaking also represent a worst-case situation at landfill sites. Even in such a situation the synthetic samples fixed with asphalt exhibited a strong resistance to leaching action; thus, in 48-hour tests, only 1.07% to 1.3% (Tables 6 and 7) of the total metals were leached. Actual waste samples from Tobyhanna Army Depot showed somewhat high, i.e., 6-20%, leaching of the total metals under the same conditions (Tables 8 and 9); however, the large excess of lime in the samples, and the consequent occurrence of the heavy metals in the hydroxide form, could have created an unfavorable condition for complete wetting and micro-encapsulation of the waste sample by the hydrophobic molten asphalt. This condition could conceivably be corrected by proper pH adjustment of the samples prior to fixation.

The most soluble pollutants present in the synthetic samples in this investigation were effectively protected from leaching, as has been the experience with water-soluble radwastes fixed with asphalt.<sup>10-12</sup> Moreover, the electroplating waste samples fixed with asphalt were not treated to reduce the  $\text{Cr}^{+6}$  to  $\text{Cr}^{+3}$  or to destroy the cyanide. These separate treatment procedures are prescribed for all electroplating wastes prepared for landfill disposal by cementation and/or containerization processes.<sup>11,12,16</sup> It has been consistently observed in the present experimental work, however, that both soluble hexavalent chromium and cyanide are effectively fixed by the WPC-VRS process, which protects them from leaching action by the acid-buffer eluent in the case of both Tobyhanna and synthetic samples. It can therefore be concluded that the electroplating waste could be adequately asphalt-fixed by micro-encapsulation, by the WPCVRS process, following pH adjustment, without pretreatment to eliminate  $\text{Cr}^{+6}$  or cyanide in any form. However, it should be emphasized that such process characteristics as size reduction of the waste salt to 20 microns, complete wetting by the molten asphalt, and complete evaporation of water, must be maintained to make the operation successful. Although the present investigation has shown that waste samples need not be treated to remove hexavalent chromium and cyanides in the asphalt fixation process these constituents should be removed, for added safety and to insure the permanence of the fixed samples and their resistance to leaching by acid buffer solutions in the landfills. Cyanide removal also destroys the cyanide complexes of cadmium and zinc, thereby contributing to the immobilization of these metals.

The results of the tests made on the Tobyhanna Army Depot samples fixed by the A.E. Peters Associates,<sup>15</sup> cement process and by the USAEHA on a modification<sup>10</sup> of that process show very low concentration values of

metal leached, less than 0.1 ppm for all metals in the A.E. Peters Associates work, and 0.2 to 0.8% in the USAEHA report. The reason for their good results, however, is that they used unbuffered distilled water as their leachant. This solvent is far less effective than natural landfill leachants, which invariably contain humic acids, partially neutralized by basic materials in the soil. The leaching test data presented by these reports are therefore far from realistic. Heavy metal hydroxides embedded in the porous cement matrices can be continuously leached by natural acid buffer solutions. It is obvious, however, that a rigorous comparison cannot be made between the asphalt and cementation processes until electroplating wastes fixed by cementation are subjected to leaching by such standard tests as the Wisconsin or other USEPA-approved toxicant extraction procedures,<sup>21</sup> which more closely simulate the natural leaching process in landfills. Moreover, such testing is logically necessary to verify the claim that asphalt fixation is 50-100 times as efficacious as the cementation process for radwastes, which are similar to electroplating wastes.<sup>7</sup>

The high leaching rate observed in the present study with asphalt-fixed TOAD wastes is a cause for concern. It can be argued that in the final disposal, the asphalt-fixed wastes are containerized in asphalt-lined drums and so prevent leachant water from entering the fixed-waste block (which can be described as a solid block of hydrophobic asphalt matrix almost completely protecting the heavy metal hydroxides). Such drums, disposed of at approved landfill sites, do not run the risk of being leached by the buffered acid leachants. Cement-fixed blocks, being hydrophilic, are more easily permeated and leached by such leachants. It would be prudent, however, to confirm, by further experimental work, that the micro-encapsulation of natural waste samples with molten asphalt can be improved and made as efficacious as the same process proved to be for the synthetic samples investigated in the present work. The possible process variables that could be addressed may be summarized as:

1. Removal and destruction of cyanide, ammonia, and other complexing ions by standard procedures to reduce the solubility of Zn, Cu, Cd, Pb, etc.
2. Segregation of the chromecontaining waste and reduction of hexavalent chromium by a standard method.
3. Control of the addition of lime to the minimum needed for complete precipitation of the heavy metals.

Apart from the actual performance of the fixing process, in terms of the percentage of metals leached by the leachant in standard tests, one can consider the actual metal concentrations in the leachate and compare them with the allowable concentrations, according to state or federal regulations. The available data are presented in Table 10. It is clear that the final concentrations of the critical metals in the leachates of the present investigation are below the limiting concentrations proposed by

TABLE 10. COMPARISON OF THE ALLOWABLE AND ACTUAL CONCENTRATION OF METALS IN ALL LEACHATES

Metal	Allowable Concentration PA Reg. a ppm	Allowable Concentration USEPA Proposed Reg. b ppm	Experimental Values ppm			
			TOAD 1	TOAD 2	Synthetic 1	Synthetic 2
Zn	3.00	3.40	4.268	1.012	0.481	1.012
Cu	0.90	4.60	2.089	0.589	0.336	0.756
Cd	1.20	1.00	19.792	2.048	0.147	1.596
Pb	--	0.80	12.766	0.722	0.181	0.608
Cr <sup>+3</sup>	3.00	3.95	0.036	0.203	0.043	0.357
Cr <sup>+6</sup>	0.14	0.25	0.036	0.023	0.007	0.007
CN <sup>-</sup> ppb	0.00	0.20	0.076	BDL	BDL	0.023

a. Reference 5.

b. Reference 22.



USEPA, and also by the Pennsylvania state government, except in the case of zinc, copper, and cadmium, the concentrations of which were slightly higher in the Wisconsin test leachate than the proposed limits. The percentage leaching values also were inordinately high in the case of these metals.

#### CONCLUSION

The Werner and Pfleiderer Corp.'s volume reduction and solidification process for fixing electroplating waste by asphalt was found to be very efficacious in case of synthetically prepared hazardous waste samples simulating the waste generated in various US Army depots. The maximum leaching by the standard modified Wisconsin<sup>13</sup> leach test was 1.1 to 1.3% of the total metals and the final metal concentrations in the leachate were within the limits specified by proposed Pennsylvania state regulations and USEPA standards for electroplating point-source categories. Hexavalent chromium and cyanide ions were also effectively attenuated by the WPC-VRS process.

In the case of actual waste samples generated at Tobyhanna Army Depot leaching was high, 6-20% of the total metals contained in the fixed samples. This deficiency was traceable to the absence of separate chemical pretreatment of samples containing chrome and cyanide before subjecting the samples to liming and asphalt fixation. Liming of the TOAD samples was also observed to be far in excess of that required. It is expected that asphalt fixation by the WPC-VRS method should work as efficaciously for TOAD samples as for synthetically prepared samples when the critical process variables have been specifically addressed. Even in case of the TOAD samples fixed by asphalt, the final concentrations of metals in the experimental leachates were lower than the specified limits with the exception of zinc, cadmium and copper.

#### RECOMMENDATIONS

Segregated chromium-containing and cyanate-containing waste should be obtained from Tobyhanna Army Depot and subjected to treatment to, respectively, reduce chromium (VI) to chromium (III) and oxidize cyanide. Controlled liming should then be carried out to precipitate the heavy metals, and this should be followed by asphalt-fixation. It is expected that the results obtained with synthetic sludges would then be reproduced.

In order to establish the comparative merits of the cementation process and the asphalt process, the USEPA-approved Wisconsin leaching test procedure, as modified in the present investigation, should be applied to the samples of waste fixed by the Chem-cementation procedures developed by A.E. Peters Associates and by USAEHA personnel. This would permit valid data to be obtained on the leaching of heavy metals from wastes solidified by the "Chem-Fix" process.



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#### LIST OF ABBREVIATIONS AND TECHNICAL TERMS

TOAD	Tobyhanna Army Depot, Pennsylvania
ppm	parts per million
mg/l	milligrams per liter
mg/kg	milligrams per kilogram
µg/l	micrograms per liter
USAEHA	United States Army Environmental Hygiene Agency
WPC-VRS	Werner and Pfleiderer Corporation - volume reduction and solidification process
RCRA	Resource Conservation and Recovery Act
BDL	Below detection level
Radwaste	Radioactive waste chemicals
Chem-Fix	The proprietary process of fixing liquid hazardous waste of A.E. Peters Associates, consisting in solidification by Portland cement and sodium silicate in a definite proportion
leachant	leaching medium
leachate	leaching medium with leached material
eluent	a leaching medium which fractionally leaches certain materials in preference to others as used in chromatography, but it is used synonymously with leaching medium in the literature on landfill leachings.
eluate	eluting medium with eluted material

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